Crossover from 180-to-90 degree domains in ferroelectric thin films

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We have grown thin films of the classical tetragonal perovskite ferroelectric PbTiO₃ on DyScO₃ substrates. Due to the minuscule mismatch between PbTiO₃ and DyScO₃ at the growth temperature (< 0.4% at 570°C), high-quality paraelectric thin films can be grown, in which periodic ferroelectric domains form upon cooling down. The thinnest of these films (d< 8nm) display 180° periodic domains due to the large depolarizing fields, whereas the thicker films (d> 28nm) consist of 90° domain patterns determined by the elastic energy. For intermediate thicknesses, we have observed for the first time the crossover from 180°-to-90°domain walls. For this crossover, we propose a model that combines the elastic and electrical boundary conditions, giving rise to ferroelectric closure-like domains.

The observed domain periodicity (Λ) versus film thickness (d) correlation, has revealed the energetics of domain wall formation. For d< 8nm, 180°domains form with periodicity in accordance with Kittel’s Law applied to ferroelectric domains (Λ~d⁻¹/²). Taking into account that during the cooling process, the domain walls can ’freeze in’[2], we have measured up to T=200°C and did not observe any changes, showing that the 180° domain ’freezing’ occurs above this temperature. Fitting the vs. d data provides domain wall energy between 120 and 132mJ/m² for freezing temperatures (Tₐ) between 200° and 440°C, respectively, which is in good agreement with ab initio calculations for free-standing PbTiO₃ [1].

The 90° domains in thicker films (d> 28nm), obey Roytburd’s Law for 90° domains, with the same d⁻¹/² dependence and domain wall formation energy between 10 (Tᵦ = 440°C) and 65mJ/m² (Tᵦ =25°C). Therefore, 90° domain walls are likely to be mobile down to room temperature [4]. This result, which is in good agreement with ab initio calculations [1] for freestanding PbTiO₃, is somewhat surprising for epitaxially grown films and is most likely due to the elastic properties of DyScO₃ [3].